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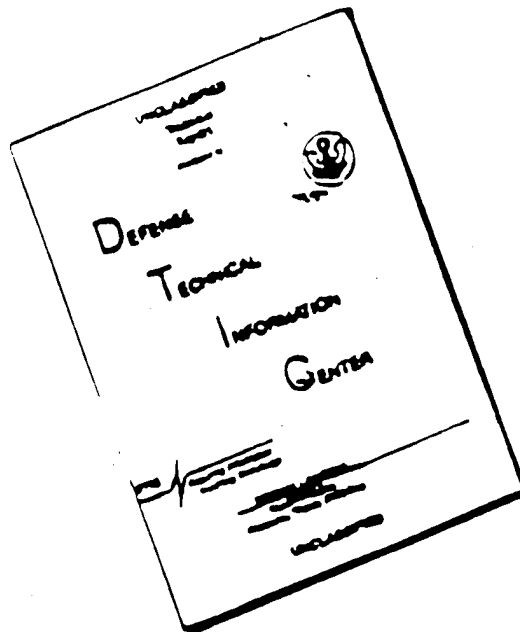
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6. AUTHOR(S) F. Mansfield, H. Xiao, L.T. Han, C.C. Lee J. Jones-Meehan, B. Little					
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**THE IMPACT OF MICROBIOLOGICALLY INFLUENCED CORROSION
ON PROTECTIVE POLYMER COATINGS**

F. Mansfeld, H. Xiao, L.T. Han, C.C. Lee
Corrosion and Environmental Effects Laboratory (CEEL)
Department of Materials Science and Engineering
University of Southern California
Los Angeles, CA 90089-0241, USA

J. Jones-Meehan
Naval Surface Warfare Center
Code R-301
Silver Spring, MD 20903

B. Little
Naval Research Laboratory
Code 7333
Stennis Space Center, MS 39529-5004

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ABSTRACT

Thirteen sets of polymer coated steel were exposed to Pacific ocean water at Port Hueneme, CA (NS) and artificial (AS) sea water in July 1994. The same types of coating systems were exposed in Key West, FL in May 1995. In this report data for three sets of coatings systems exposed at Port Hueneme and in the laboratory are discussed. Each set had a different primer - metallic zinc, IVD-Al or phosphate. Within each set one group of samples had an epoxy coating, the other group had an additional layer of polyurethane as a topcoat. Degradation of the protective properties of the polymer coatings was followed by recording impedance spectra and electrochemical potential and current noise data as well as by visual observation. Impedance data were collected at the remote test site once a week and noise data twice a week via modem from the laboratory at USC. Preliminary statistical analyses concerning the effects of the nature of the primer, presence of a topcoat and exposure medium (biotic vs. abiotic) were performed based on the breakpoint frequency f_b obtained from impedance data and the noise resistance R_n and the spectral noise resistance R_{sn}^0 obtained from noise data. Samples exposed to three different colonies of microorganisms containing sulfate reducing-bacteria (SRB) and a control solution were evaluated using electrochemical impedance spectroscopy (EIS). Selected samples were examined by environmental scanning electron microscopy (ESEM) to determine biofilm distribution and spatial relationships between coating damage and microorganisms.

Keywords: polymer coatings, natural seawater, microbial corrosion, EIS, ENA, laboratory tests, surface analysis.

INTRODUCTION

The impact of microorganisms on corrosion protection by polymer coatings is being evaluated at present for thirteen different coating systems on steel during exposure to natural Pacific seawater at Port Hueneme, California. Additional tests have been initiated at Key West, Florida in May 1995. Previous studies by Jones-Meehan et al [1,2] indicated that mixed cultures containing SRB could cause degradation of the protective properties of polymer coatings. In the present study coating performance is being evaluated by analysis of impedance spectra and electrochemical noise data. Electrochemical impedance spectroscopy (EIS) has been shown to be a powerful non-destructive tool for the evaluation of coating properties and their changes with exposure time [3-6]. The application of electrochemical noise analysis (ENA) is relatively new [7]. Results obtained with EIS and ENA in laboratory tests for two of the coatings systems studied in the present project have been discussed elsewhere [8-10].

Since impedance and noise measurements have to be performed for a large number of samples at remote test sites (Port Hueneme, CA and Key West, FL), it was necessary to develop a new approach for monitoring of coating properties [7,11]. Experiments were performed by an on-site computer controlled via modem by a computer system at CEEL/USC using software developed for this purpose. Since simultaneous collection of potential and current noise data requires a two-electrode system [7-10], impedance data were collected for the same system. To illustrate the experimental approach developed for remote monitoring of coating performance using EIS and ENA, data obtained during exposure to natural seawater (NS) at Port Hueneme and to artificial (AS) seawater at CEEL/USC for several coating systems with different performance will be presented in the following.

Coating degradation due to the presence of microorganisms in sea water is being determined for two different series of coating systems. In the CR series different types of primes, midcoat and topcoat have been applied. Results obtained for these coating systems in the early stages of exposure have been discussed elsewhere [12,13]. The JJ series of coatings was designed to allow evaluation of the effects of different primers (metallic zinc, IVD aluminum and phosphate) and an additional polyurethane topcoat over an epoxy midcoat on coating performance in general and attack by microorganisms in particular. The nature of the metallic primer changes the potential of the steel/coating system and might affect interactions with microorganisms. In the following, only data obtained for the JJ series will be discussed. Coated steel samples were removed from AS and NS when the rusted area exceeded 0.1 - 0.3% of the total area as determined by visual observation. Samples removed from NS were subjected to analysis with an environmental scanning electron microscope (ESEM) to determine biofilm distribution and spatial relationships between coating damage and microorganisms.

The impact of different cultures of SRB on coating performance was studied in laboratory experiments [12]. After different exposure periods the coating properties were evaluated with EIS. Exposed samples were also analyzed with ESEM.

EXPERIMENTAL APPROACH

1. Materials and Methods

Materials

Several types of marine coatings applied on steel were exposed to AS and NS. Coating degradation and corrosion occurring at the metal/coating interface were studied by EIS and ENA and by visual observation. The composition and average coating thickness of the six types of coating systems to be discussed in the following are listed in Table I. Coatings were applied by AAA Plating, Compton, CA according to the specifications listed in Table I. Coating systems JJ1 and JJ2 had metallic zinc, JJ3 and JJ4 had phosphate, and JJ5 and JJ6 had IVD-aluminum applied on the top of the steel substrate. All JJ coatings had an epoxy polyamide primer (two layers) as midcoat and JJ2, JJ4 and JJ6 had a polyurethane topcoat (Table I). Coated steel samples were 15 cm (6") by 10 cm (4") rectangular coupons for sea water exposure and 7.6 cm (3") by 7.6 cm (3") for exposure to bacteria in laboratory tests. The exposed area for each coupon was about 250 cm² in AS and NS exposures. Care was taken to protect the edges of each coupon by applying an additional thick layer of epoxy polymer along the edges. A wire was attached to the bare steel at the middle of one short edge providing electrical connection and mounting support.

Exposure Conditions

Two samples of each JJ coating system were exposed to AS in a 130 liter water tank for up to one year in laboratory tests at CEEL and to Pacific Ocean water at the Naval Civil Engineering Facilities, Port Hueneme, CA. The Pacific ocean water flowed through the tank continuously at a rate of about 0.5 l/min. Arrangements were made for the sea water to drip into and out of the tank to avoid grounding problems [7].

In the laboratory study concerning the impact of different microorganisms on coating performance, the coating systems were exposed to three different marine, mixed communities containing SRB. Samples measured 4" x 4" for the CR series and 3" x 3" for the JJ series. Isolation, maintenance and characterization of the SRB communities have been described elsewhere [1,2,14,15]. All communities were grown anaerobically at room temperature in sealed containers. The CG-59 mixed community contained hydrogenase-negative SRB originally isolated from corroding seawater piping. The 49Z mixed community contained hydrogenase-positive SRB originally isolated from 4340 steel coupon with a zinc plate primer that was located in a constant seawater immersion flume tank. The P14 mixed community contained hydrogenase-positive SRB isolated from a 4340 steel coupon with a 5-step iron phosphate primer and epoxy topcoat that was located in a constant seawater immersion flume tank. As a control the coated samples were exposed to a sterile medium.

Methods

Impedance and electrochemical noise data were measured using a two-electrode arrangement as described previously for the simultaneous collection of noise data (Fig. 1) [7-11]. The necessity of collecting data by remote control at the sea water test site led to development of a new approach for monitoring of the properties of polymer coatings during exposure to seawater [7,11]. Each sample pair occupied one input channel of a multiplexer (Fig. 2) which is a 2 x 20 switch unit. Each input channel had two electrically isolated leads which were switched together either into connection or disconnection with the two leads of the main output. Whenever a channel was switched in, the two leads of the multiplexer main output were in connection with the two

samples of the pair which occupies that channel. The isolation resistance between the two leads of a channel and between channels was greater than $10^{10} \Omega$.

The voltmeter and the potentiostat formed the electrochemical noise measurement unit. The general approach for simultaneous collection of potential and current noise was the same as discussed previously [7-11]. When a pair of coated samples was switched into connection with the noise measurement unit, the potentiostat applied 0 mV potential difference between the two samples (Fig. 1). Current fluctuations between the pair were measured by the potentiostat. One lead of the voltmeter was switched into connection with one of the samples, while the other lead was connected to the Ag/AgCl reference electrode. Since the potential difference between the two samples was 0 mV, the voltmeter measured the potential fluctuations of the couple vs. the reference electrode. A modified version of the previously developed noise data acquisition software [7-11] was used to control the multiplexer as well as the voltmeter and the potentiostat for simultaneous sampling of potential and current fluctuations at a rate of 2 points/sec.

For impedance measurements an approach which differs from the traditional scheme had to be used (Fig. 2) [7,11]. The poor high frequency (>100 Hz) current response of the multiplexer caused distortion of the ac signals when the impedance measurements were performed using a potentiostat. Therefore a Solartron model 1255 frequency response analyzer (FRA) with a signal generator and two analyzers was applied for impedance measurements (Fig. 2). When a coated sample pair was switched into connection with the FRA, an accurate resistor was placed in series with the sample pair. The voltage signal generated by the FRA was applied across the coupon pair and the resistor. The response to the signal applied across the sample pair was determined by one analyzer and compared with the total voltage signal measured by the other analyzer. Since the value of the resistor was known, the impedance of the coated sample pair could be calculated. For decreasing frequencies the initial resistor was replaced automatically by a series of other resistors with higher values. A newly developed impedance data acquisition program was used for collecting the data and controlling the FRA.

All measurement operations were fully controlled by computer programming, including input channel switching, instrument synchronization, noise and impedance data collection. In any measurement, only one input channel was allowed to switch into connection with main output. In noise measurements, only the voltmeter and the potentiostat can be connected with the multiplexer main output, while during impedance measurements, the main output is only in connection with the FRA without connection to the noise unit. In this way, either noise or impedance data were measured only once for one pair of coated samples at any given time.

A modem was installed inside the computer at the marine test site to control the measurement and allow corrosion monitoring by remote control. Both the computer at CEEL/USC and the remote-site computer were installed with compatible modems and corresponding communication software for computer communication through a telephone line. Software and hardware arrangements allowed the two computers to be connected through the telephone line. As a result, the computer at CEEL/USC took control over the remote-site computer and the keyboard and screen at the CEEL/USC computer became the same as the those of the remote-site computer. Therefore measurements could be set up at CEEL/USC and data collected at the marine site could be transferred to the laboratory.

In the laboratory tests the instrumentation was basically the same as at the Port Hueneme site except that the multiplexer and modem were not used. A Solartron model 1286 or a PAR 273A potentiostat and a Solartron model 1250 FRA were used to determine the electrochemical data.

Electrochemical noise data were collected twice a week and impedance spectra were measured once a week. Samples were usually removed when the visual rating according to ASTM D 610 had dropped below 8 (few isolated rust spots, less than 0.1% rusted area) and were evaluated by ESEM.

Polymer coated panels were removed from either natural seawater or laboratory media and shipped from UCS to NRL/SSC in the electrolyte to which they had been exposed in a lucite container made to accommodate the panels in an upright, separated position. Specimens were removed and placed in 4% glutaraldehyde in filtered seawater at 4°C for a minimum of four hours followed by removal of residual salts by rinsing through a series of filtered seawater/distilled water washes. ESEM examination was performed in an Electroscan (Wilmington, MA) Type II microscope. Specimens were attached to a Peltier stage maintained at 4°C and imaged in an environment of water vapor at 2-5 torr to maintain samples in a hydrated state. The ESEM was operated at 20 keV using the environmental secondary detector. EDS data were obtained with a NORAN (Middleton, Wisconsin) Series II analyzer equipped with a beryllium window detector. Samples were held at a 20° tilt during spectrum acquisition. A program correcting for atomic number (Z) absorption (A), and fluorescence (F) was used for semiquantitative analysis during data acquisition.

2. Data Analysis

Electrochemical Data. Due to the large number of samples and exposure times and the fact that not all samples have been removed at present due to insufficient coating degradation, only a qualitative analysis of the EIS data has been performed so far. In general it has been observed that the model to be used for quantitative analysis of the impedance behavior of the coated steel samples needed to be changed from the general coating model [5,6] at shorter exposure times to a model which considers the influence of mass transport in pores of the coatings and in rust spots [7]. The breakpoint frequency f_b [5,6] has been determined from all spectra and used for the preliminary statistical analysis described below.

From the electrochemical noise data the noise resistance $R_n = \sigma\{V(t)\}/\sigma\{I(t)\}$ defined as the ratio of the standard deviation of the potential noise $\sigma\{V(t)\}$ and the current noise $\sigma\{I(t)\}$ and the spectral noise resistance $R_{sn}^0 = \lim_{f \rightarrow 0} \{R_{sn}(f)\}$, where R_{sn} is the spectral noise response at

$$f \rightarrow 0$$

frequency f [7-11], have been determined and used in the statistical analysis of the experimental data. While R_n is determined by statistical analysis of the experimental data in the time domain, R_{sn}^0 is obtained by analysis in the frequency domain.

Statistical Analysis. One-way and two-way analyses of variance (ANOVA) are statistical techniques to identify the significance of the impact of changing one or two experimental conditions on experimental results. When data are grouped according to different experimental conditions, ANOVA calculates a statistical coefficient F for each experimental effect [16]:

$$SS = \sum_i X_i^2 - \frac{\left(\sum_i X_i\right)^2}{N} \quad [1]$$

$$df = N - 1 \quad [2]$$

$$MS = \frac{SS}{df} \quad [3]$$

$$F = \frac{MS_B}{MS_R} \quad [4]$$

where SS is the sum of squares, X_i are the experimental data used for the analysis, N is the total number of data points, df is the degrees of freedom, MS is the mean square value, MS_B is the mean square value between data groups, and MS_R is the mean square value within data groups (residual variance). The F value must be compared with a tabulated critical value F_{crit} , which is a positive number depending on the degrees of freedom and the confidence level [16,17]. Conclusions can be drawn at a certain confidence level (which determines F_{crit}) depending on whether F is smaller or larger than F_{crit} . A two-way ANOVA has two F values representing each experimental effect under test. The ANOVA test only predicts the significance of the effects of different experimental conditions. ANOVA was applied to f_b values obtained after three months exposure and longer to determine the impact of microorganisms as well as types of primers and different types of midcoat and topcoat layers on coating degradation.

EXPERIMENTAL RESULTS AND DISCUSSION

All JJ coating systems had two layers of epoxy as midcoats, the odd number series of coatings (JJ1, JJ3 and JJ5) had no topcoat, while the even number series of coatings (JJ2, JJ4 and JJ6) had an additional polyurethane topcoat. The primer for JJ1 and JJ2 was metallic zinc, for JJ3 and JJ4 it was phosphate, and for JJ5 and JJ6 was IVD aluminum (Table I). Comparison of the results obtained with EIS and ENA during exposure to seawater allowed an evaluation of the effects of the nature of the primer (zinc vs. phosphate vs. Al), presence of the polyurethane topcoat and the effect of microorganisms on polymer degradation in NS. Due to the large number of experimental data and different coating systems a statistical approach was taken to obtain this information. Samples removed from the exposure tests were observed in the ESEM in order to provide information concerning the location of bacteria with respect to observed coating damage.

Problems were encountered in visually rating coating degradation according to ASTM D 610 mainly due to the use of metallic primers in which case rust spots were not observed as long as Zn or Al provided cathodic protection despite of corrosion at the metal/coating interface. The impedance behavior of these primers exposed through pinholes in the coatings probably affected the measured impedance spectra of the polymer coated steel samples and caused deviations from the coating model used previously to analyze impedance spectra for polymer coated steel [5,6]. Fig. 3 gives a comparison of JJ2 and JJ4 samples after exposure to NS for 405 days. No rust spots were visible on JJ2 which has a metallic zinc primer (Fig. 3a). This made visual rating unreliable in assessing the damage level of the coating, since the rating relies on the observation of substrate corrosion products (yellow to brown rust for steel substrate) at damaged coating sites. To simplify the present analysis process, only f_b , R_n and $R_{o_{sn}}$ were used in analyzing the results obtained so far for the JJ series coatings. A more detailed analysis will be performed when all samples have been removed.

Zinc concentrations obtained by EDS could not be used to detect breaches in JJ2 coatings, because all coatings produced EDS spectra consistent with 2 - 3% Zn.

1. Exposure to Natural and Artificial Seawater

JJ1 and JJ2. Fig. 4a and b show impedance spectra for JJ1 after 1, 4 and 7 months exposure in NS and AS, respectively. The impedance spectra, especially for samples in NS, most likely contain contributions from the corrosion reaction of Zn under the porous polymer coatings. In addition, formation of calcareous deposits is possible since E_{corr} remained below -850 mV at all times. The impedance spectra for JJ2 in AS and NS are shown in Fig. 5. More complicated spectra with lower impedance values were found for coupons exposed to NS. JJ1 coupons exposed in NS and AS initially had f_b values around 100 Hz, but in AS f_b increased to about 1000 Hz after 7 months exposure, indicating that coating degradation and corrosion were more severe in AS than in NS (Fig. 6). On the other hand, for JJ2 f_b values obtained from spectra in NS were much higher than those for AS suggesting that the JJ2 coating degraded more in NS than in AS (Fig. 6). JJ2 coatings exposed to NS were colonized by filamentous bacteria (Fig. 7a) and diatoms (Fig. 7b). E_{corr} for JJ1 and JJ2 in AS and NS exposure showed very similar trends and remained around -1000 mV vs Ag/AgCl due to exposure of metallic Zn in pre-existing and developing pores in the coating (Fig. 8). Visual observation did not show rust spots, indicating that the steel substrate remained cathodically protected. R_n and $R_{\text{O}_{\text{sn}}}$ for JJ1 coupons exposed to AS were initially higher than for exposure in NS, but after seven months similar values were observed (Fig. 9a). R_n and $R_{\text{O}_{\text{sn}}}$ decreased with time in AS and to a lesser extent in NS reaching similar values after 7 months (Fig. 9a). For JJ2 samples exposed to AS, R_n and $R_{\text{O}_{\text{sn}}}$ fluctuated around $10^6 \Omega$ ($2.5 \times 10^8 \Omega \text{ cm}^2$) and were about one order of magnitude higher than R_n and $R_{\text{O}_{\text{sn}}}$ for exposure in NS (Fig. 9b).

JJ2 had the lowest f_b values in AS and the highest values in NS (Fig. 6). The overall trend of the f_b data suggests that in NS coating degradation was more severe for JJ2 than for JJ1, while the opposite result occurred in AS. Apparently, the polyurethane topcoat provided extra corrosion protection in AS, but not in NS exposure. R_n and $R_{\text{O}_{\text{sn}}}$ values were higher for JJ2 than for JJ1 in AS, but had similar values in NS (Fig. 9). It will be noted that R_n and $R_{\text{O}_{\text{sn}}}$, which are obtained by different methods of data analysis, were similar in AS, but always showed lower values for R_n in NS (Fig. 9).

JJ3 and JJ4. The impedance spectra for JJ3 exposed in AS and NS shown in Fig. 10 have a complicated frequency dependence. Impedance values decreased with time for all coupons exposed in AS and NS indicating similar coating degradation. For JJ4 coupons, the impedance spectra obtained in AS and in NS showed little coating degradation (Fig. 11). Impedance values were much higher than those obtained for JJ3 coupons (Fig. 10). In AS f_b for JJ3 coupons increased from about 0.1 Hz to 500 Hz, while in NS, f_b values increased from about 1 Hz to 100 Hz (Fig. 12). It seems that the JJ3 coating degraded slightly more in AS than in NS. The JJ4 coupons had similar f_b values in AS and in NS which increased only slowly with time (Fig. 12).

E_{corr} values for JJ3 in AS and NS exposure decreased from -300 mV to -600 mV in first three weeks and then remained more or less constant with time (Fig. 13). More positive E_{corr} values were found for JJ4 in both AS and NS exposure (Fig. 13). R_n and $R_{\text{O}_{\text{sn}}}$ values for JJ3 in AS fluctuated and reached similar levels as in NS after 5 months (Fig. 14a). R_n values were slightly lower than $R_{\text{O}_{\text{sn}}}$ in both AS and NS. For JJ4, R_n and $R_{\text{O}_{\text{sn}}}$ values obtained in AS and in NS had similar values and fluctuated around $10^6 \Omega$ ($2.5 \times 10^8 \Omega \text{ cm}^2$) (Fig. 14b), with R_n being slightly lower than $R_{\text{O}_{\text{sn}}}$ in almost all cases.

In AS and in NS exposure the visual rating grades decreased from 9.5 to 8 for one JJ3 coupon and from 9.5 to 8.5 for the other. The decreasing rating grades indicated the occurrence of small rust spots. Since the phosphate primer did not provide cathodic protection, coating damage

resulted in corrosion of the steel substrate. The visual rating grades for JJ4 coupons in AS and NS were all above 9.5 as no rust spots were observed.

JJ4 had lower f_b values in AS and NS than JJ3, indicating that the JJ4 coating performed better than JJ3, which is consistent with the visual rating results. For longer exposure periods the higher f_b values in AS seem to indicate poorer performance. After about 6 months, R_n and $R_{o_{sn}}$ values for JJ4 were higher than for JJ3 in AS and NS exposure (Fig. 14). At this time similar values of R_n and $R_{o_{sn}}$ were observed for AS and NS exposure of both JJ3 (Fig. 14a) and JJ4 (Fig. 14b).

JJ5 and JJ6. The impedance spectra for JJ5 for exposure in AS and in NS are shown in Fig. 15. In AS, the spectra for JJ5 exhibited a high-frequency time phase angle minimum at all exposure times, but the dc limits were still quite high (Fig. 15b). The impedance spectra in NS did not show this high-frequency time constant feature (Fig. 15a). The impedance spectra for JJ6 coupons exposed in AS and in NS showed capacitive behavior with high impedance values indicating good coating performance during the entire exposure period (Fig. 16).

The f_b values for JJ5 and JJ6 in AS and in NS were low and did not change very much with time (Fig. 17). E_{corr} increased from about -900 to about -600 mV in both AS and NS for JJ5 (Fig. 18). For JJ6 E_{corr} increased from about -900 to about -300 mV in the first four months and then decreased again to -800 mV at the end of exposure in NS. In the first three months E_{corr} remained much lower for exposure in AS for both JJ5 and JJ6 indicating a slower rate of degradation of the Al primer (Fig. 18). R_n and $R_{o_{sn}}$ for JJ5 fluctuated with lower values in NS for the initial exposure period during which E_{corr} was higher in NS (Fig. 19a). Generally R_n values were slightly lower than $R_{o_{sn}}$, especially for coupons in NS. For JJ6 R_n and $R_{o_{sn}}$ fluctuated around $10^6 \Omega$ ($2.5 \times 10^8 \Omega \text{ cm}^2$) in both AS and NS with $R_{o_{sn}}$ values being slightly higher than R_n values (Fig. 19b).

2. Exposure to Mixed Communities of Bacteria

After exposure to three different marine, mixed communities containing sulfate-reducing bacteria (SRB) and a control solution impedance spectra were collected in AS. In most cases, spectra were obtained for the entire immersed sample ($A = 105 \text{ cm}^2$). Since it was observed that damage was often more severe at the edges of the coated samples despite the extra paint layer, EIS were also determined for an area of 20 cm^2 on each flat side of a sample for certain exposure times. Data for one month exposure have been discussed elsewhere [12,13]. No definite conclusions have been reached so far from analysis of EIS data for these samples since considerable variations in coating degradation occurred for different exposure times. This problem is illustrated in Fig. 20 which shows impedance spectra for JJ5 after about one year exposure. Except for exposure to the solution containing 49Z bacteria, two samples were available. While the impedance for the two control samples was the highest, large differences were observed for the two samples. For samples exposed to bacteria, severe attack had occurred and the coating was partially removed. Coating degradation was most severe for JJ5. For the JJ6 coating damage was only indicated for the control sample and the sample exposed to the solution containing CG-59 bacteria (Fig. 21).

DISCUSSION

Table II lists the results of an overall qualitative evaluation of corrosion damage levels for the JJ series of coatings after 7 months exposure based on the data obtained from electrochemical tests and visual observation. JJ1 showed more severe corrosion in AS than in NS. JJ3 showed

some moderate corrosion of steel since cathodic protection was not provided by the primer. For JJ2 in AS as well as for JJ4, JJ5 and JJ6 only light levels of corrosion damage were observed.

The JJ series of coatings was designed to have different combinations of three types of primers with the same epoxy midcoat, with or without a polyurethane topcoat. The nature of the primer also determines the open-circuit potential which affects formation of calcareous deposits and may influence the extent to which microorganisms are attached to polymer surfaces in NS.

Comparison of JJ1 and JJ2. Formation of calcareous deposits in pores of the coatings may have contributed to the complex shapes of the impedance spectra for JJ1 and JJ2 in AS and NS (Fig. 4 and 5). Comparison of the time dependence of f_b for JJ1 and JJ2 (Fig. 6) showed that JJ2 performed better than JJ1 in AS, while in NS JJ2 degraded slightly more than JJ1. Further comparison showed slightly higher R_n and $R_{o_{sn}}$ values in the first six months for JJ1 in AS than in NS, while for JJ2 R_n and $R_{o_{sn}}$ were significantly lower in NS than in AS (Fig. 9). The polyurethane topcoat seemed to enhance the protective properties of the epoxy coating in AS, while in NS it apparently degraded more rapidly leading to degradation of the epoxy midcoat. Although partially degraded, the polyurethane topcoat provided an additional diffusion path (the coating on JJ2 was 56% thicker than that on JJ1 (Table I)) resulting in lower corrosion rates for JJ2 compared to JJ1 as qualitatively represented by $1/R_n$ and $1/R_{o_{sn}}$.

The results of the two-way ANOVA are shown in Table III for JJ1 and JJ2 in AS and NS. The low F values for 'Solution' and 'Coating' compared to $F_{crit} = 7.05$ at the 99% confidence level suggest that neither the exposure environment (AS vs NS) nor the polyurethane topcoat (JJ1 vs JJ2) made significant systematic impact on corrosion resistance of the coated steel. However, the very high F value for 'Interaction' indicates a strong interaction between the effect of the environment and the effect of the topcoat which means that the performance difference between JJ1 and JJ2 is significantly different in AS and NS. The difference between the effects of the exposure medium (AS and NS) is significantly different for JJ1 from that for JJ2. This result could be explained by assuming that microorganisms plugged some of the pores of the coating on JJ1 making the observed coating performance appear slightly better than in AS. However, since polyurethane is susceptible to biodegradation [18,19], the degradation of the polyurethane topcoat caused JJ2 to perform worse in NS than in AS.

Comparison of JJ3 and JJ4. The f_b values for JJ3 were more than 50 times higher than those for JJ4 in AS, while in NS f_b values for JJ3 were at least 10 times higher than those for JJ4 (Fig. 12) indicating that JJ3 degraded more than JJ4 in AS and NS exposures. Comparison of visual rating grades also indicated increasing extent of corrosion for JJ3, but not for JJ4.

The results of a two-way ANOVA are shown in Table IV. The F value for 'Solution' was less than $F_{crit} = 7.05$ at the 99% confidence level suggesting that exposure in AS or NS did not produce significant differences of the protective properties of the coatings on JJ3 and JJ4. The F value for 'Coating' was higher than F_{crit} indicating that the polyurethane topcoat had a significant effect on corrosion protection in both AS and NS exposure. The small F value for 'Interaction' means that the effect of the environment and the effect of the polyurethane topcoat did not interfere with each other significantly. The performance difference between JJ3 and JJ4 in AS probably did not differ significantly from that in NS. In other words, the performance difference for JJ3 in AS and NS may not be significantly different from that for JJ4 in AS and NS. The microorganisms did not seem to affect the coating performance significantly possibly due to the improved adhesion between coating layers caused by the phosphate primer.

Comparison of JJ5 and JJ6. The IVD-Al primer on JJ5 and JJ6 has been reported to provide good adhesion and adequate cathodic protection [20]. Inspection of the results in Table II

shows that JJ5 and JJ6 experienced only minor degradation of the protective properties of the coating system.

A two-way ANOVA was performed using f_b values for JJ5 and JJ6 exposed in AS and NS (Table V). The F value for 'Solution' was much higher than F_{crit} meaning JJ5 and JJ6 performed differently in AS and NS. The high F value for 'Coating' suggested significant differences between the corrosion behavior of JJ5 and JJ6 in both AS and NS. The F value for 'Interaction' was also high, indicating that the coating performance difference between JJ5 and JJ6 in AS was not the same as that in NS, or in other words, the effect of the exposure environment (AS vs NS) on coating performance of JJ5 was significantly different from that of JJ6. A reasonable explanation drawn from the ANOVA is that JJ6 performed much better than JJ5 in AS because of the presence of the polyurethane topcoat, while in NS the performance of JJ6 was not significantly better than that of JJ5, because of biodegradation of the polyurethane topcoat.

Comparison of All JJ Series Coatings. In order to evaluate the performance of the epoxy coating with and without the polyurethane topcoat in AS and NS, a two-way ANOVA was performed using f_b values for all coupons. Four groups were categorized for the analysis: epoxy/AS (JJ1, JJ3 and JJ5 in AS), epoxy/NS (JJ1, JJ3 and JJ5 in NS), epoxy+polyurethane/AS (JJ2, JJ4 and JJ6 in AS), and epoxy+polyurethane/NS (JJ2, JJ4, JJ6 in NS). The ANOVA results in Table VI showed that the F values were very small for 'Solution' and 'Coating' compared with $F_{crit} = 6.76$ at the 99% confidence level, which means that the JJ series coatings as a whole showed little difference during exposure to AS or NS. Considering the individual comparison results for AS and NS exposure, it was found that the polyurethane topcoat did not provide significant improvement of corrosion resistance in NS. However, the large F value for 'Interaction' indicated that the effect of the polyurethane topcoat (JJ1,3,5 vs JJ2,4,6) was significantly different between AS and NS exposures, indicating that microbiological effects were significantly different for epoxy and epoxy+polyurethane coatings. A reasonable explanation is that the polyurethane topcoat slightly improved corrosion resistance compared to that provided by epoxy layers alone in AS, but since polyurethane can be affected by microorganisms [18,19], the polyurethane layer did not provide significant additional corrosion protection in NS.

The improvements of corrosion resistance provided by different primers were relatively easier to see. Phosphate layers improve the adhesion between the steel and the coating, but the porous phosphate layer is more easily penetrated resulting in steel corrosion. A considerable number of rust spots was found on JJ3 in AS and NS, but fewer were found on JJ4 (Table II), indicating that the lack of cathodic protection is a disadvantage of the phosphate primer in the absence of a topcoat. On the other hand, metallic Zn and IVD-Al primers provided cathodic protection for JJ1, JJ2, JJ5 and JJ6. In terms of base steel corrosion protection, Zn and IVD-Al primers performed better than the phosphate primer. The corrosion processes evaluated by the electrochemical techniques for JJ1, JJ2, JJ5 and JJ6 were the dissolution process of Zn (JJ1 and JJ2) or Al (JJ5 and JJ6). In order to determine the significance of differences between Zn and IVD-Al primers, two-way ANOVA were performed comparing JJ1 with JJ5 and comparing JJ2 with JJ6 in AS and NS. The F value for 'Coating' effect was higher than F_{crit} for JJ1 and JJ5 (Table VII) indicating that there were differences in coating performance between JJ1 and JJ5. The exposure and interaction effects were not strong (Table VII) because microorganisms apparently did not affect the epoxy midcoat. Comparisons of f_b (Fig. 6 and 17) and R_n and $R_{o_{sn}}$ values (Fig. 9 and 19) indicated that dissolution of Al was less severe than that of Zn. For the ANOVA of JJ2 and JJ6 (Table VIII), the F values for 'Solution', 'Coating' and 'Interaction' were all very high indicating (i) significant differences between the performance of JJ2 and JJ6, (ii) significant effects of exposure environments for both JJ2 and JJ6 and (iii) strong interactions between these two effects. The differences in coating performance could be seen by comparing f_b , R_n and $R_{o_{sn}}$ (Fig. 6 and 17) values for JJ2 and JJ6 (Fig. 9 and 19) showing that JJ6 performed better than JJ2 in AS and NS. The strong effect of the exposure medium is possibly due to biodegradation of the

polyurethane topcoat on both JJ2 and JJ6 in NS. The strong interaction effect means that biodegradation of polyurethane for JJ2 was different compared to JJ6. The result that the polyurethane topcoat degraded more for JJ2, which has a metallic Zn primer in NS, than for JJ6 with an IVD-Al primer, points to the open-circuit potential having a significant effect on coating performance. A more detailed analysis of the mechanism of degradation of the coating properties of the JJ series will only be possible when the results for all samples have been analyzed after an exposure period of at least one year.

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Table III Results of Two-way ANOVA for Comparison of Exposure in AS and NS for JJ1 and JJ2

<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>
Solution	494521.5	1	494521.5	3.990213
Coating	148945.8	1	148945.8	1.201819
Interaction	7557417	1	7557417	60.97956
Within	7931751	64	123933.6	
Total	16132636	67		

Table IV Results of Two-way ANOVA for Comparison of Exposure in AS and NS for JJ3 and JJ4

<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>
Solution	69019.78	1	69019.78	5.672268
Coating	233434.2	1	233434.2	19.18437
Interaction	66236.8	1	66236.8	5.443553
Within	778747.8	64	12167.93	
Total	1147439	67		

Table V Results of Two-way ANOVA for Comparison of Exposure in AS and NS for JJ5 and JJ6

<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>
Solution	1.11634	1	1.11634	51.45908
Coating	0.335374	1	0.335374	15.45946
Interaction	0.381376	1	0.381376	17.57999
Within	1.3884	64	0.021694	
Total	3.221489	67		

Table I. Composition and Thickness of Coating Systems (JJ Series)

Sample Name	JJ1	JJ2	JJ3	JJ4	JJ5	JJ6
Substrate	Cold Rolled Steel	Cold Rolled Steel	Cold Rolled Steel	Cold Rolled Steel	Cold Rolled Steel	Cold Rolled Steel
Primer	Zinc plate ^a	Zinc plate ^a	Phosphate coat ^d	Phosphate coat ^d	IVD-Al ^e	IVD-Al ^e
Midcoat	Epoxy ^b	Epoxy ^b	Epoxy ^b	Epoxy ^b	Epoxy ^b	Epoxy ^b
Topcoat		Polyurethane ^c		Polyurethane ^c		Polyurethane ^c
Ave. thickness (μm)	53	83	43	76	81	81

NOTE:

- a. Zinc plate per QQ-Z-325 Rev. C (Type II , Class 2).
- b. 2 coats of epoxy polyamide primer MIL-P-23377 Rev. F (Type I class 3) per MIL-F-18264 REV.D AMD.I.
- c. 1 coat of MIL-C-85285 REV.B (AS) AMD.2 polyurethane per MIL-F-18264 REV.D AMD.1 color #36375 lusterless gray of FED-STD-595.
- d. Phosphate coat DOD-P-16232 REV.F (Type Z class 3) ; hydrogen embrittlement relieved for 8 hours at 210-225 degree.
- e. IVD aluminum per MIL-C-83488-C (Notice 1, Type II Class I)

Table II. Corrosion Damage Evaluation of Polymer Coating Coupons Exposed to AS and NS for 7 months

Samples	A S		N S	
	#1	#2	#1	#2
JJ1	S-	S	M+	M+
JJ2	L+	L+	M	M+
JJ3	M	M-	M-	L+
JJ4	L	L+	L	L
JJ5	L+	L	L+	L
JJ6	L	L-	L	L

The damage level is categorized by the following symbols: L : Light; M : Moderate; S : Severe; + : More Severe; - : Lighter

Table III Results of Two-way ANOVA for Comparison of Exposure in AS and NS for JJ1 and JJ2

<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>
Solution	494521.5	1	494521.5	3.990213
Coating	148945.8	1	148945.8	1.201819
Interaction	7557417	1	7557417	60.97956
Within	7931751	64	123933.6	
Total	16132636	67		

Table IV Results of Two-way ANOVA for Comparison of Exposure in AS and NS for JJ3 and JJ4

<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>
Solution	69019.78	1	69019.78	5.672268
Coating	233434.2	1	233434.2	19.18437
Interaction	66236.8	1	66236.8	5.443553
Within	778747.8	64	12167.93	
Total	1147439	67		

Table V Results of Two-way ANOVA for Comparison of Exposure in AS and NS for JJ5 and JJ6

<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>
Solution	1.11634	1	1.11634	51.45908
Coating	0.335374	1	0.335374	15.45946
Interaction	0.381376	1	0.381376	17.57999
Within	1.3884	64	0.021694	
Total	3.221489	67		

Table VI Results of Two-way ANOVA for Comparison of Exposure in AS and NS for Epoxy (JJ1, 3, 5) and Epoxy+Polyurethane (JJ2, 4, 6) Coatings

<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>
Solution	64992.52	1	64992.52	0.607639
Coating	3187.917	1	3187.917	0.029805
Interaction	3011658	1	3011658	28.15708
Within	21391833	200	106959.2	
Total	24471672	203		

Table VII Results of Two-way ANOVA for Comparison of Exposure in AS and NS for JJ1 and JJ5

<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>
Solution	1044667	1	1044667	8.629858
Coating	2433710	1	2433710	20.10455
Interaction	1048092	1	1048092	8.658152
Within	7747371	64	121052.7	
Total	12273840	67		

Table VIII Results of Two-way ANOVA for Comparison of Exposure in AS and NS for JJ2 and JJ6

<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>
Solution	2980348	1	2980348	1034.494
Coating	3789054	1	3789054	1315.199
Interaction	2978832	1	2978832	1033.967
Within	184382.3	64	2880.973	
Total	9932617	67		



JJ2 sample (a) and JJ4 sample (b) after exposure to natural seawater for 405 days.

Figure 3

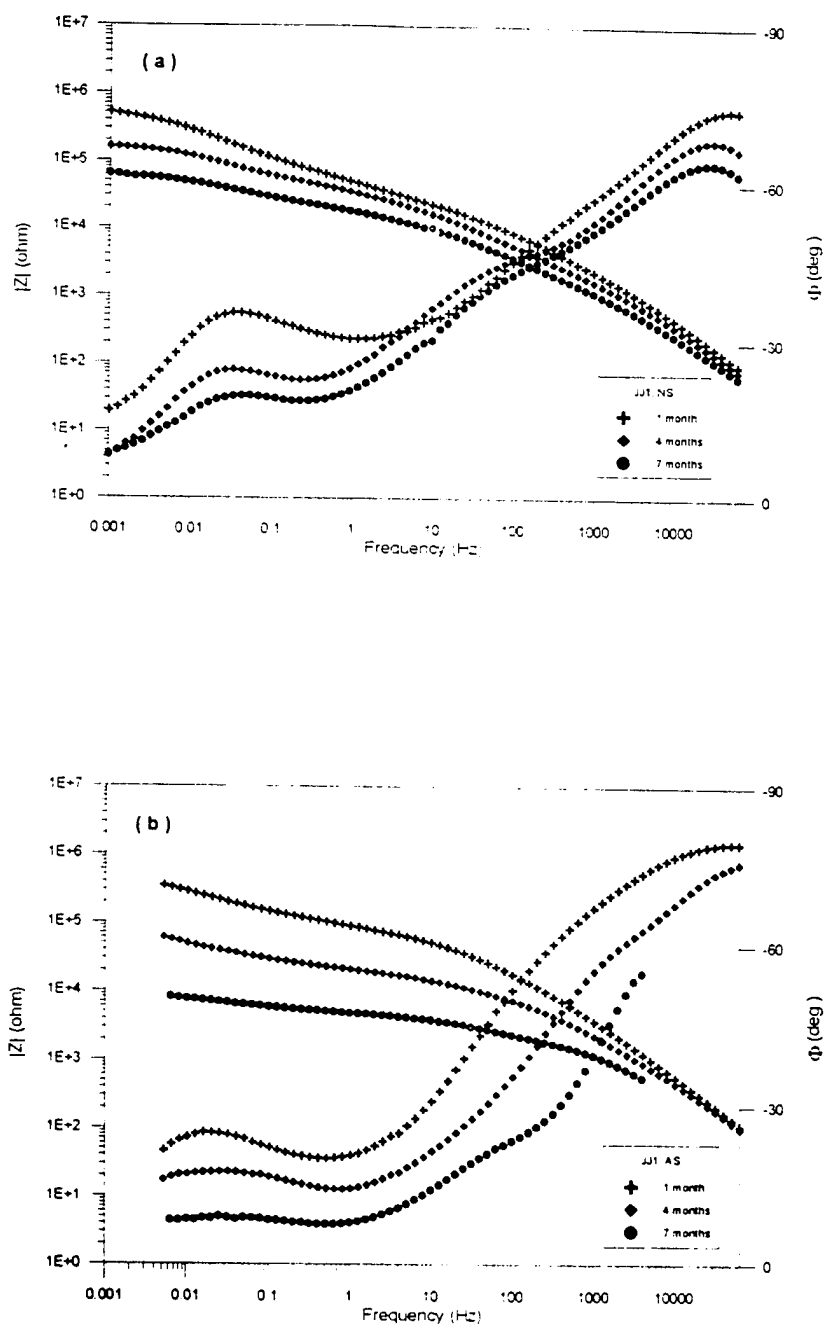


Fig. 4. Impedance spectra for coating system JJ1 exposed to natural (NS) (Fig. 4a) and artificial (AS) (Fig. 4b) seawater.

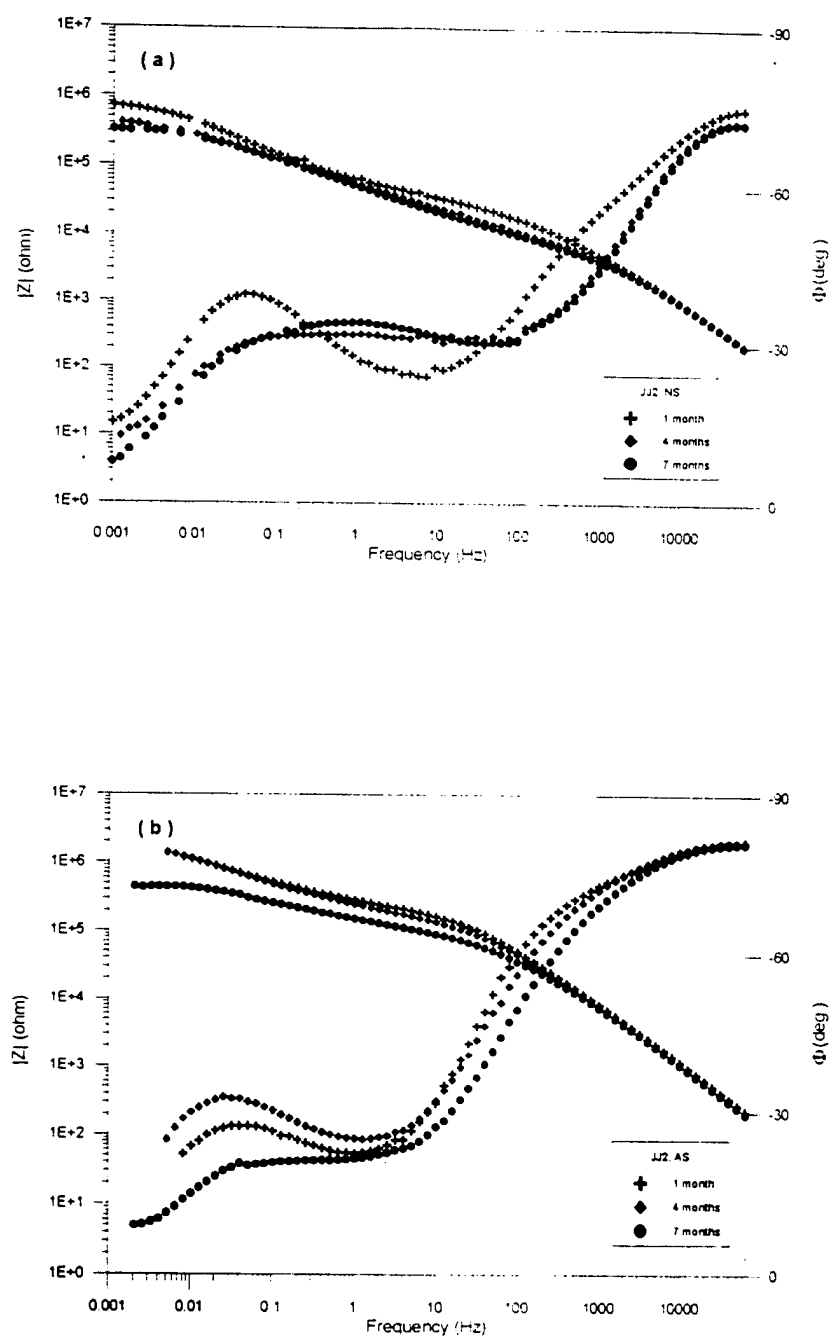


Fig. 5. Impedance spectra for coating system JJ2 exposed to NS (Fig. 5a) and AS (Fig. 5b).

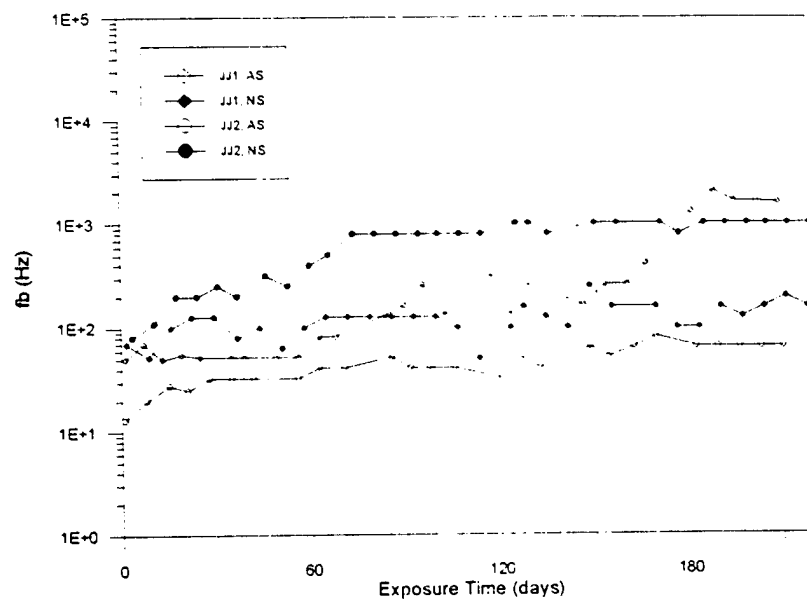
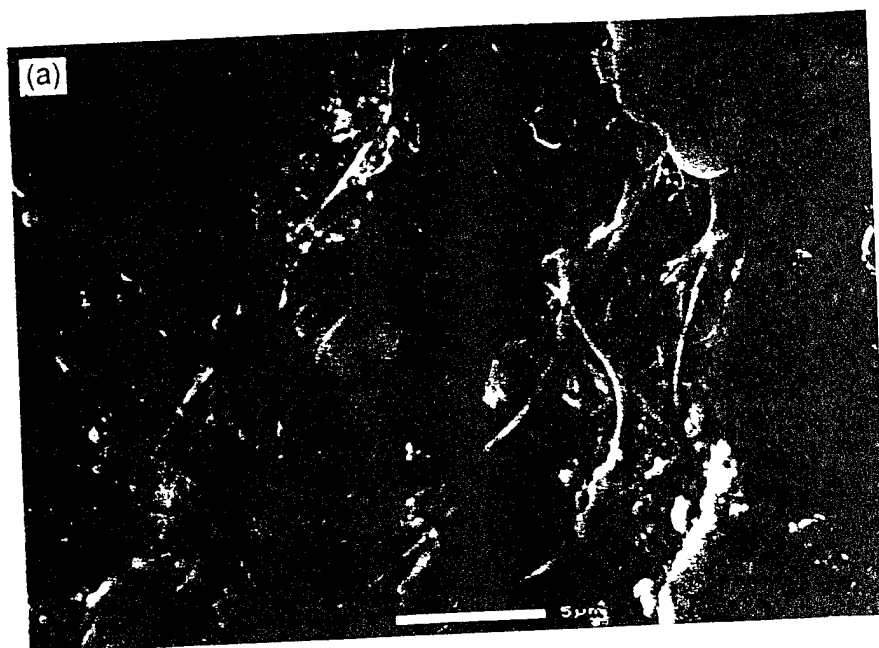


Fig. 6. Time dependence of breakpoint frequency f_b for JJ1 and JJ2 exposed to AS and NS.



JJ2 samples showing colonization by filamentous bacteria (a) and diatoms (b) after exposure to NS.

Figure 7

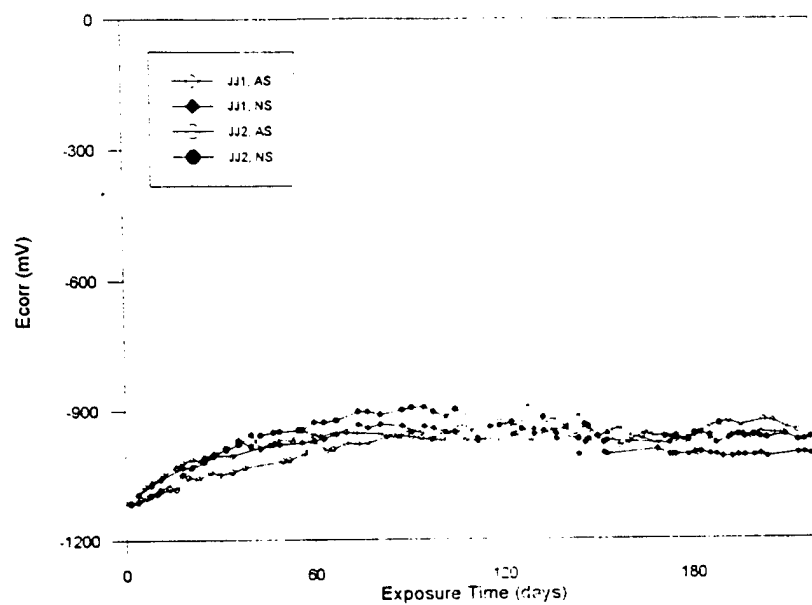


Fig. 8. Time dependence of E_{corr} for JJ1 and JJ2 exposed to AS and NS.

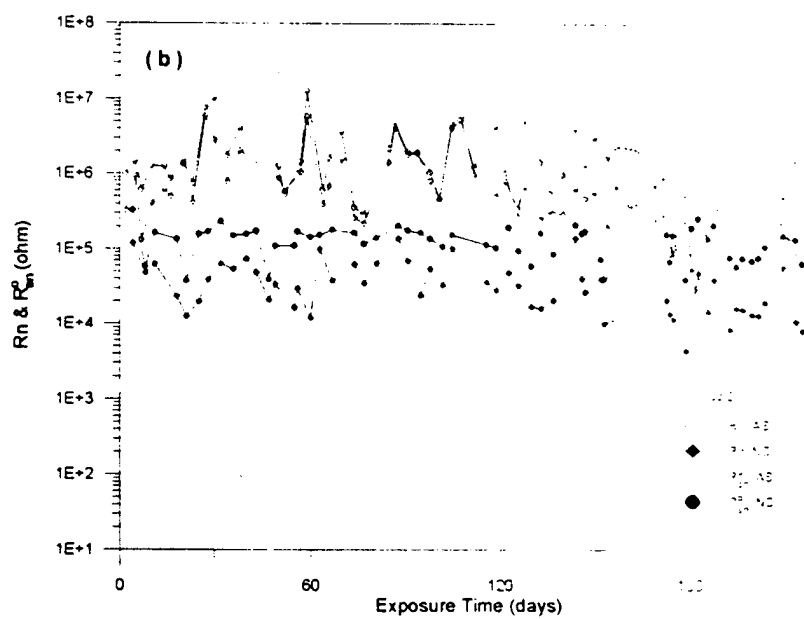
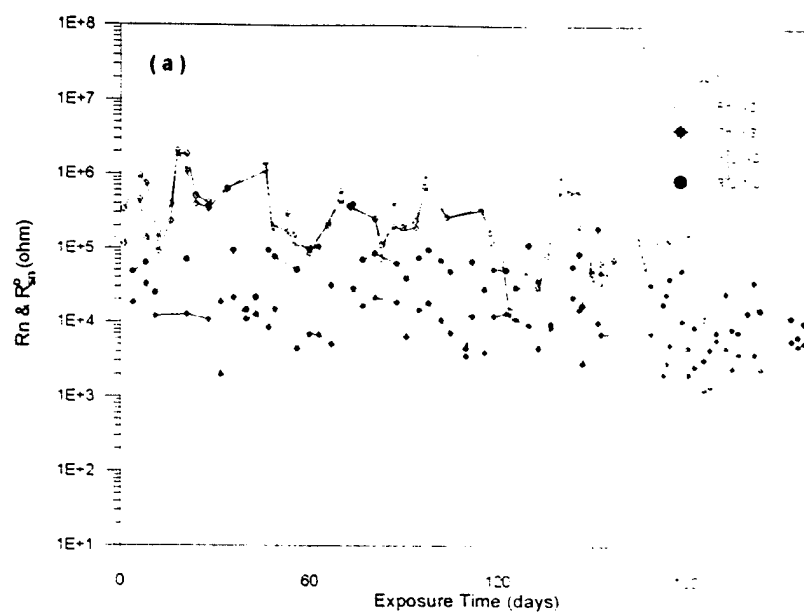


Fig. 9. Time dependence of R_n and R_{sn}^0 for JJ1 (Fig. 9a) and JJ2 (Fig. 9b) exposed to AS and NS.

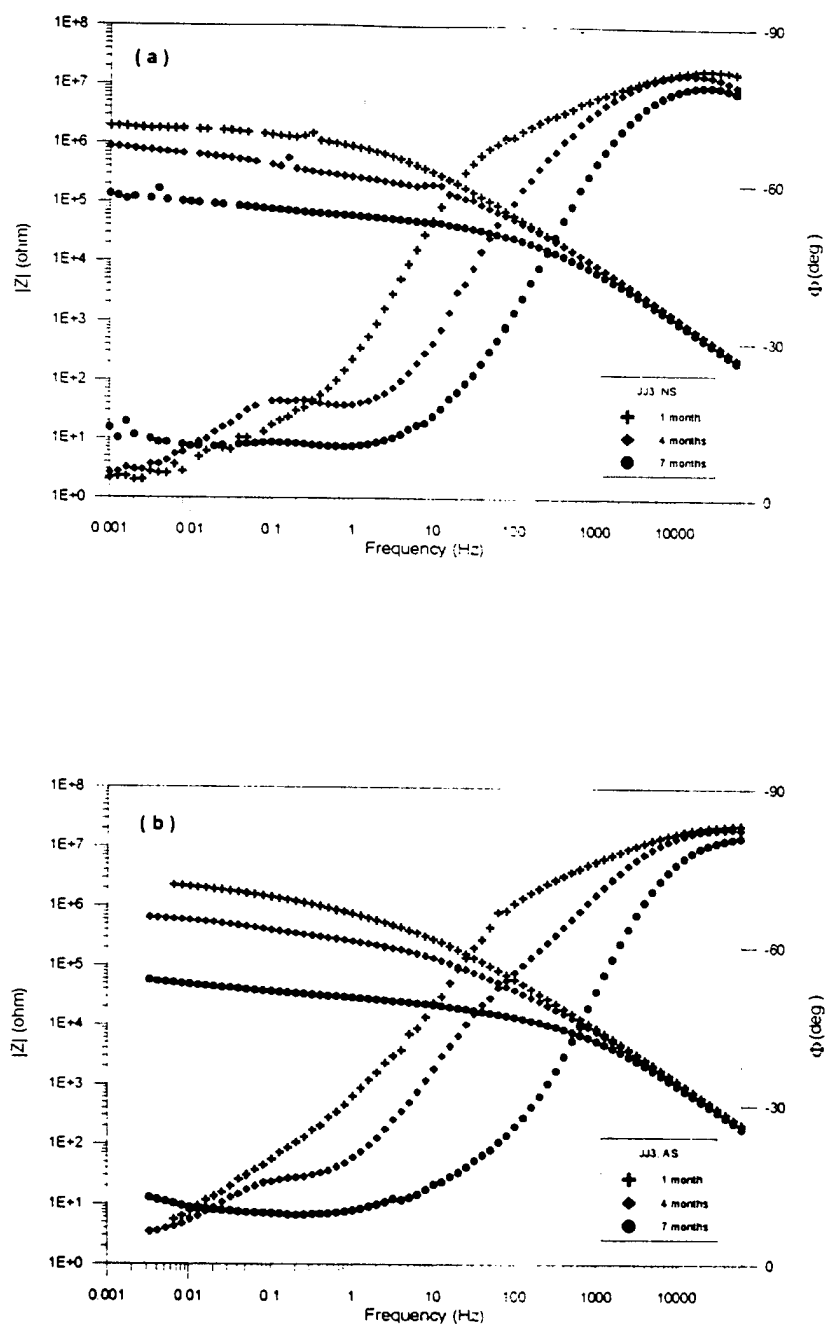


Fig. 10. Impedance spectra for coating system JJ3 exposed to NS (Fig. 10a) and AS (Fig. 10b).

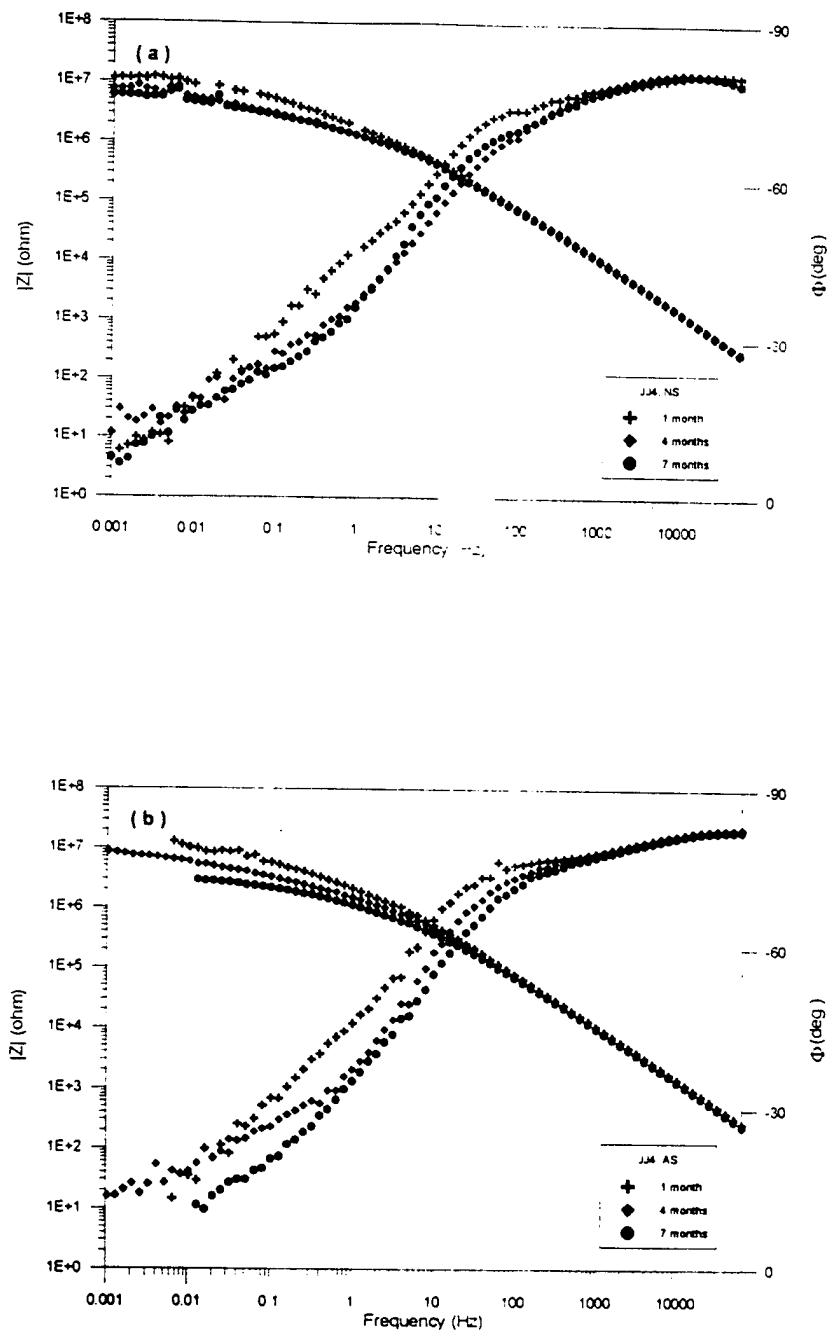


Fig. 11. Impedance spectra for coating system JJ4 exposed to NS (Fig. 11a) and AS (Fig. 11b).

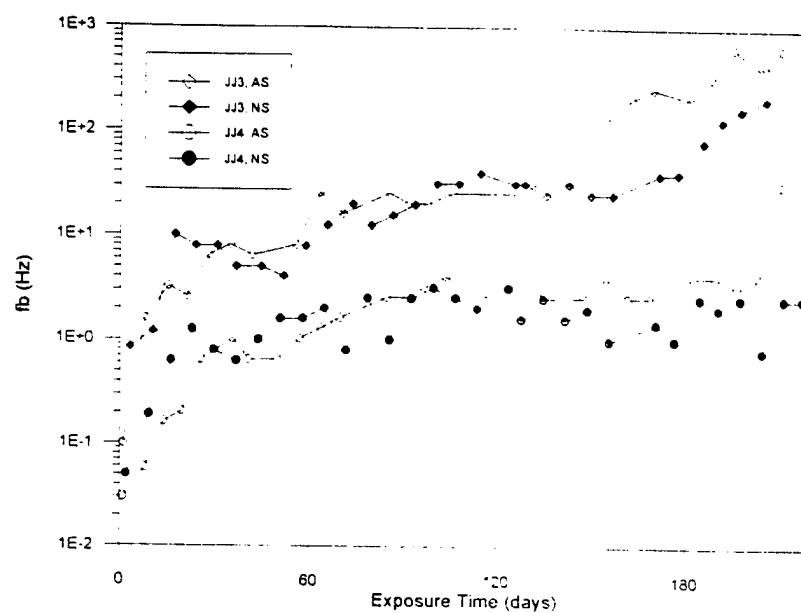


Fig. 12. Time dependence of breakpoint frequency f_b for JJ3 and JJ4 exposed to AS and NS.

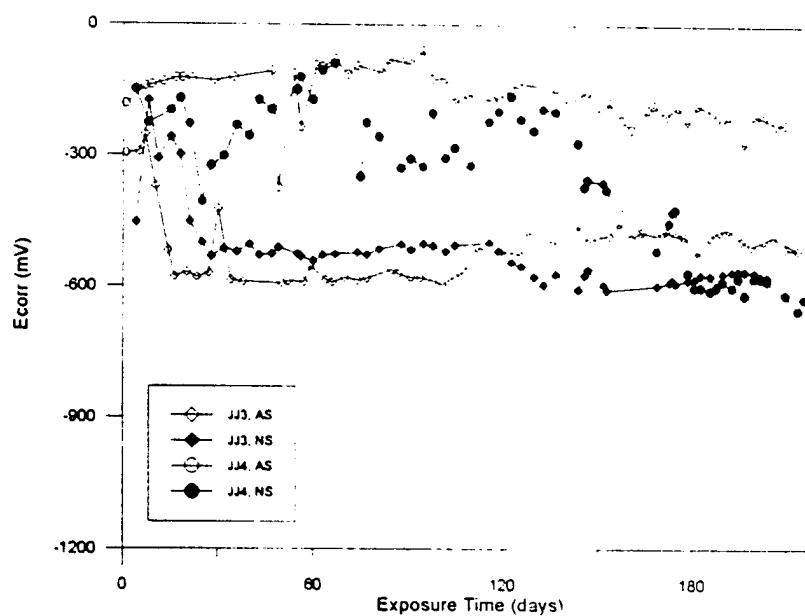


Fig. 13. Time dependence of E_{corr} for JJ3 and JJ4 exposed to AS and NS.

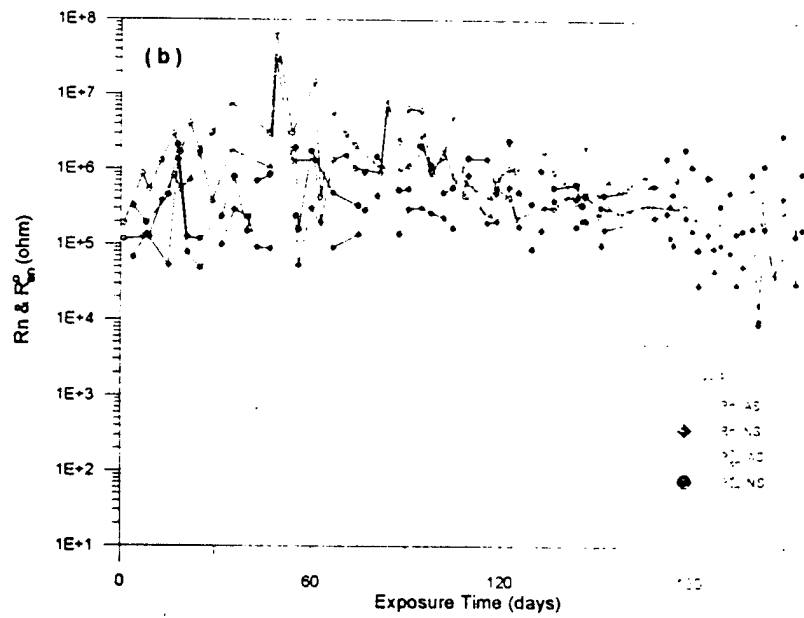
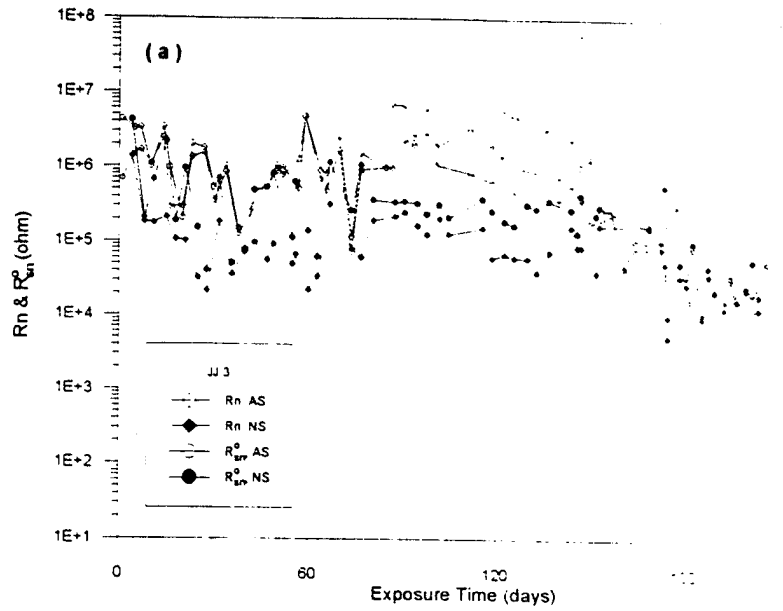


Fig. 14. Time dependence of R_n and R_{sn}^0 for JJ3 (Fig. 14a) and JJ4 (Fig. 14b) exposed to AS and NS.

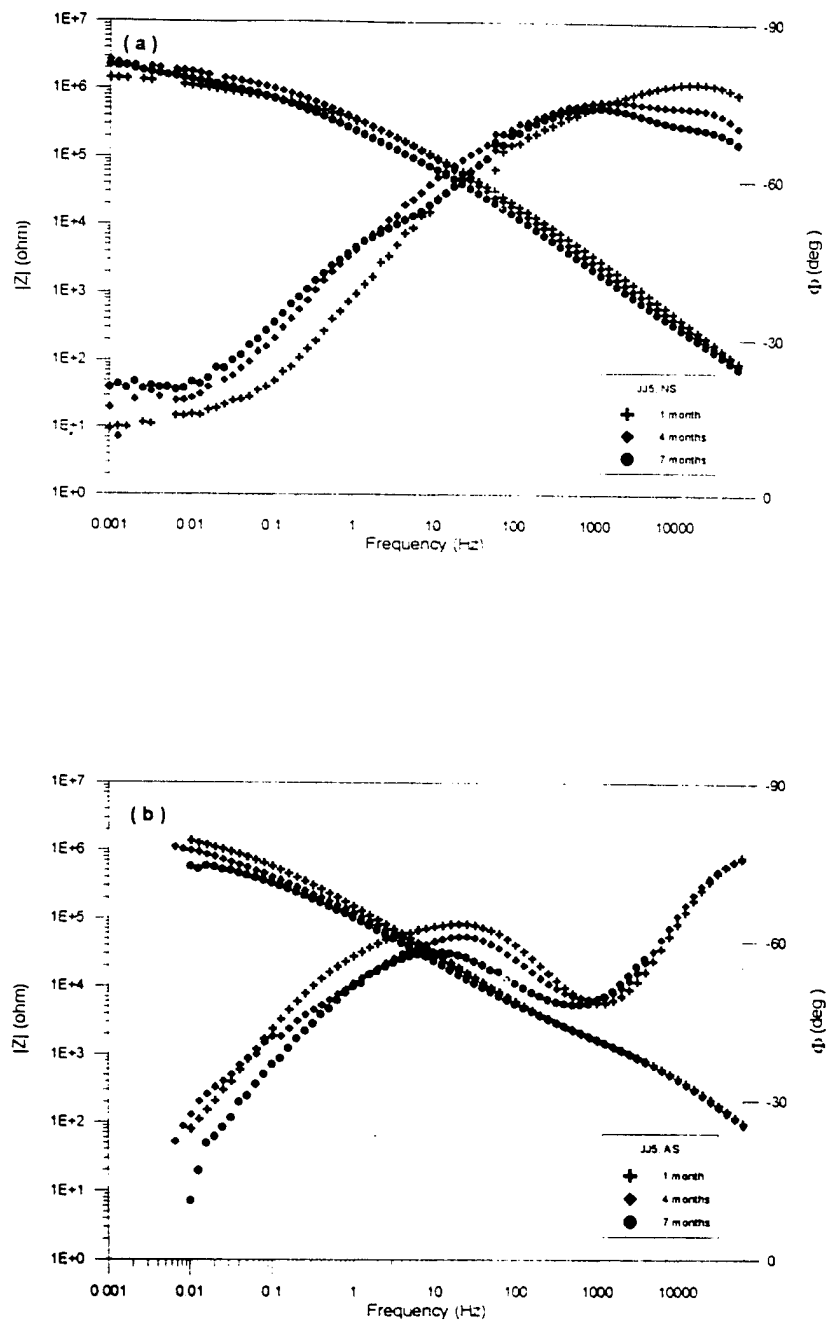


Fig. 15. Impedance spectra for coating system JJ5 exposed to NS (Fig. 15a) and AS (Fig. 15b).

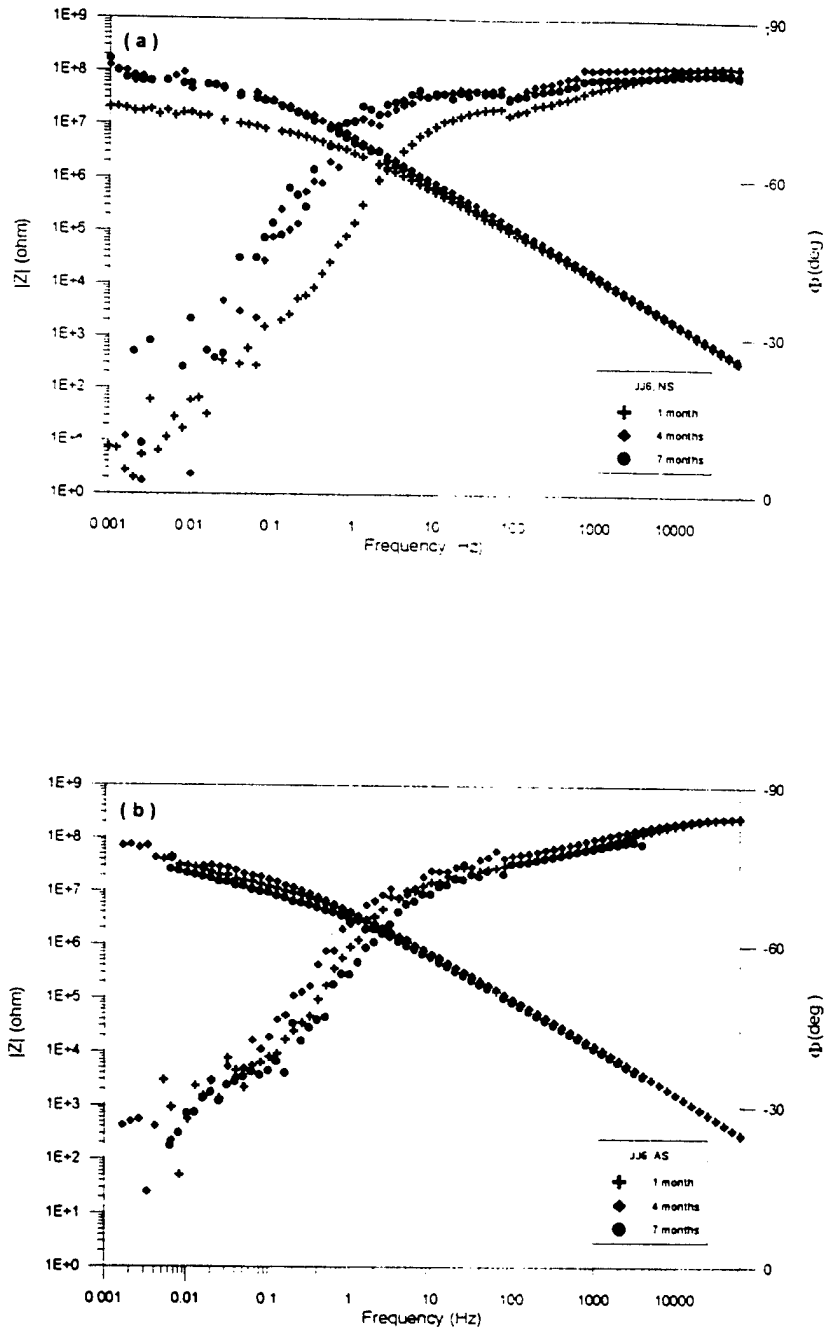


Fig. 16. Impedance spectra for coating system JJ6 exposed to NS (Fig. 16a) and AS (Fig. 16b).

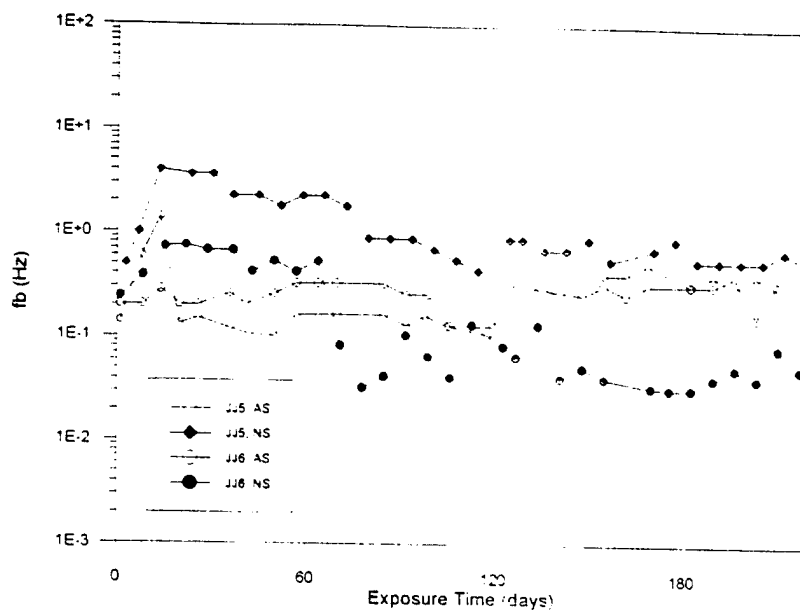


Fig. 17. Time dependence of breakpoint frequency f_b for JJ5 and JJ6 exposed to AS and NS.

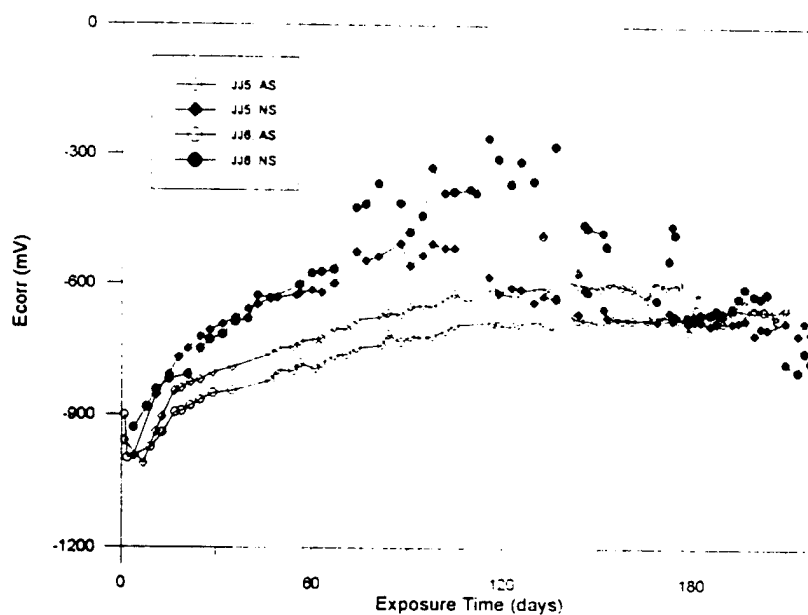


Fig. 18. Time dependence of E_{corr} for JJ5 and JJ6 exposed to AS and NS.

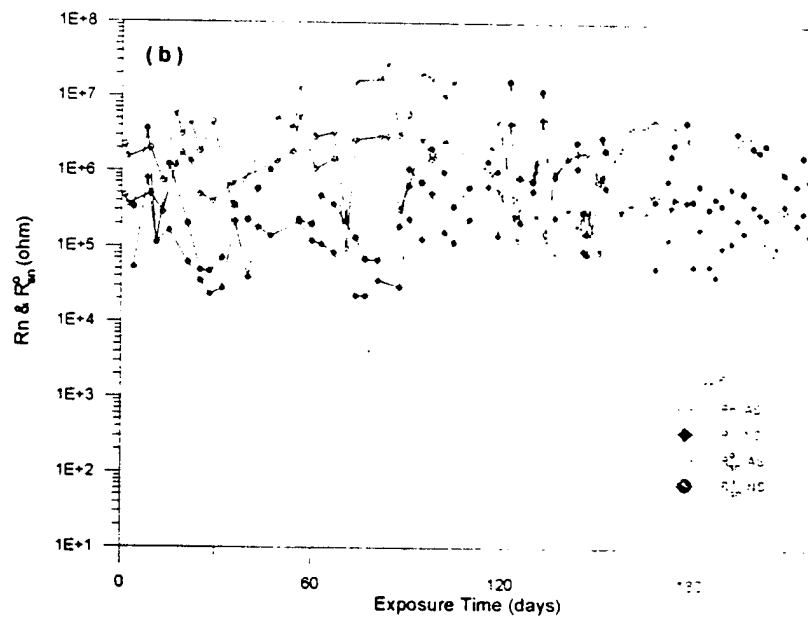
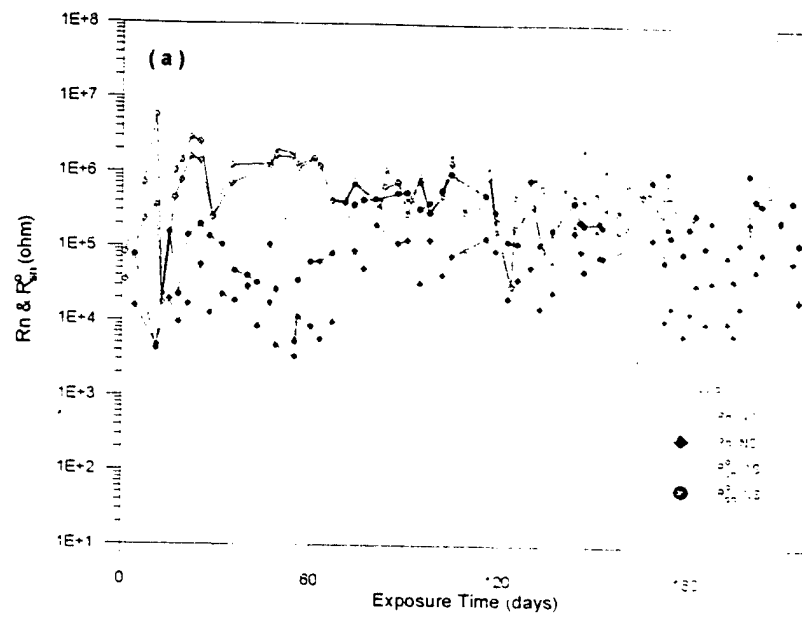


Fig. 19. Time dependence of R_n and R_{sn}^0 for JJ5 (Fig. 19a) and JJ6 (Fig. 19b) exposed to AS and NS.

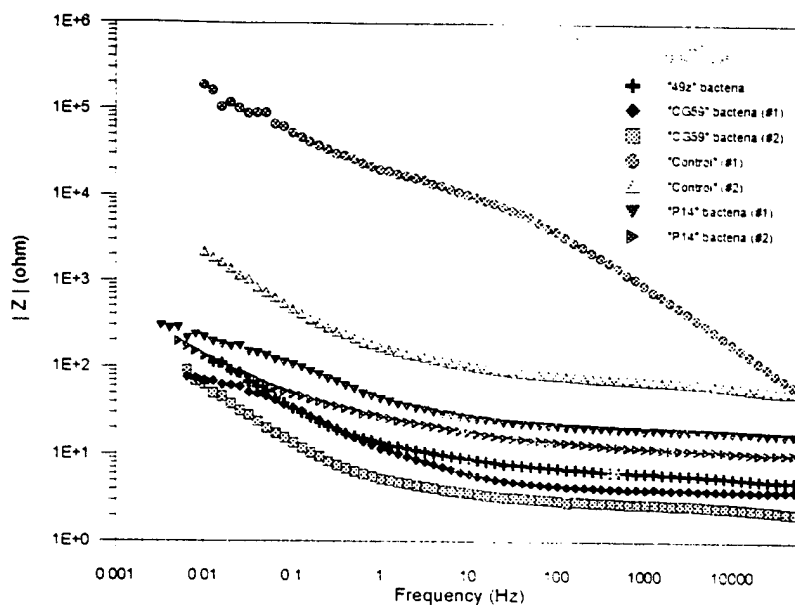


Fig. 20. Impedance spectra obtained in AS for coating system JJ5 exposed to different solutions containing bacteria and a control solution.

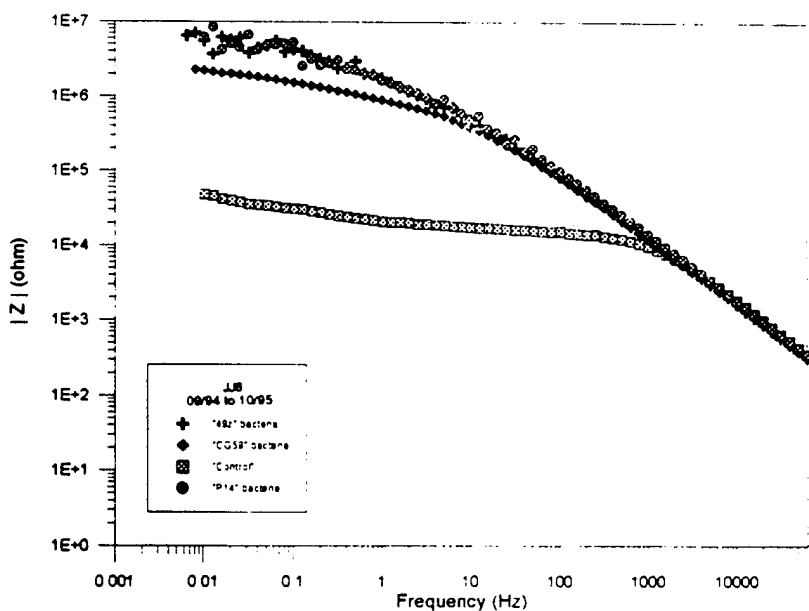


Fig. 21. Impedance spectra obtained in AS for coating system JJ6 exposed to different solutions containing bacteria and a control solution.